

# Nitrogen hydrides and the H<sub>2</sub> ortho-to-para ratio in dark clouds

V. Dislaire<sup>1</sup>, P. Hily-Blant<sup>1</sup>, A. Faure<sup>1</sup>, S. Maret<sup>1</sup>, A. Bacmann<sup>1</sup>, and G. Pineau des Forêts<sup>2</sup>

<sup>1</sup> Université Joseph Fourier and CNRS, Institut de Planétologie et d'Astrophysique, Grenoble, France  
e-mail: pierre.hily-blant@obs.ujf-grenoble.fr

<sup>2</sup> Université Paris-Orsay and CNRS, Institut d'Astrophysique Spatiale, Orsay, France

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## ABSTRACT

Nitrogen-bearing species are common tracers of the physical conditions in a wide variety of objects, and most remarkably, in dark clouds. The reservoir of gaseous nitrogen is expected to be atomic or molecular, but none of the two species are observable in the dark gas. Their abundances therefore derive indirectly from those of N-bearing species through chemical modelling. The recent years have accumulated data that stress our incomplete understanding of the nitrogen chemistry in dark cloud conditions. To tackle this problem of the nitrogen chemistry in cold gas, we have revised the formation of nitrogen hydrides, which is initiated by the key reaction  $N^+ + H_2 \rightarrow NH^+ + H$ . We propose a new rate for this reaction that depends on the ortho-to-para ratio of H<sub>2</sub>. This new rate allows reproduction of the abundance ratios of the three nitrogen hydrides, NH, NH<sub>2</sub>, and NH<sub>3</sub>, which are observed towards IRAS 16293-2422, provided that the channel leading to NH from the dissociative recombination of N<sub>2</sub>H<sup>+</sup> is not closed at low temperature. The ortho-to-para ratio of H<sub>2</sub> is constrained to O/P = 10<sup>-3</sup> by the abundance ratio NH:NH<sub>2</sub>, which provides a new method of measuring O/P. This work stresses the need for reaction rates at the low temperatures of dark clouds, and for branching ratios of critical dissociative recombination reactions.

**Key words.** astrochemistry – ISM: abundances

## 1. Introduction

Chemistry in an astrophysical context is not only a topic in itself, but it also provides invaluable tools for determining physical conditions, such as volume density and kinetic temperature (Bergin & Tafalla 2007). Astrochemistry relies on chemical networks that depend on the type of environment (e.g. diffuse vs. dense gas). The kinetic rates of the reactions are, in the best cases, based on thermodynamical and quantum mechanical calculations and experiments, which make the setup of these chemical networks an extremely demanding process. Various networks of reactions are publicly available (KIDA, UMIST, OSU<sup>1</sup>, Flower & Pineau des Forêts<sup>2</sup> 2003), with various degrees of complexity and/or completeness regarding specific aspects of the chemistry (e.g. deuteration, cations, etc.).

The nitrogen element is among the fifth or sixth most abundant in the solar neighbourhood, after H, He, C, O, and probably Ne (Asplund et al. 2009; Nieva & Simón-Díaz 2011). In the cold neutral medium, nitrogen is expected to be predominantly atomic or molecular, but direct observations of N or N<sub>2</sub> are not possible. The amount of gaseous nitrogen thus relies on the abundances of N-bearing molecules via chemical models. Nitrogen bearing molecules are observed in a wide variety of physical conditions. Molecules such as CN, HCN, and HNC, with large permanent dipole moments, are detected towards diffuse clouds (Liszt & Lucas 2001), dense cores (Tafalla et al. 2004), protoplanetary disks (Kastner et al. 2008), and high-*z* galaxies (Guélin et al. 2007). N-bearing species, such as N<sub>2</sub>H<sup>+</sup> (and its deuterated isotopologues), are also efficient tracers of the dense and cold gas where CO has already frozen out

(Crapsi et al. 2007; Hily-Blant et al. 2008, 2010b). The cyanide radical CN is also a precious molecule that serves as a tracer of the magnetic fields through Zeeman splitting (Crutcher et al. 2010). Understanding the chemistry of nitrogen is thus crucial in many astrophysical areas.

Ammonia and N<sub>2</sub>H<sup>+</sup> are daughter molecules of N<sub>2</sub>, which itself forms from atomic N through neutral-neutral reactions mediated by CN and NO (Pineau des Forêts et al. 1990). The formation of CN and the related HCN and HNC molecules, and in particular their abundance ratio CN:HCN, are however not fully understood (Hily-Blant et al. 2010b). The formation of ammonia in dark and dense gas is thought to take place in the gas phase. Once N<sub>2</sub> exists in the gas phase, it reacts with He<sup>+</sup> ions formed by cosmic-ray ionization, to form N<sup>+</sup> which by subsequent hydrogen abstractions lead to NH<sub>4</sub><sup>+</sup> and finally NH<sub>3</sub> by dissociative recombination. Le Bourlot (1991, LB91 below) was the first to investigate the influence of the H<sub>2</sub> ortho-to-para ratio (noted O/P) on the formation rate of NH<sub>3</sub>. LB91 considered the conversion between *p*-H<sub>2</sub> and *o*-H<sub>2</sub> through proton exchange in the gas phase. He concluded that when O/P ≥ 10<sup>-3</sup>, the formation of ammonia no longer depends on the value of O/P. However, a better test of the nitrogen chemistry is provided by the simultaneous observations of all three nitrogen hydrides, NH, NH<sub>2</sub>, and NH<sub>3</sub> (e.g., Persson et al. 2010). The *Herschel*/HIFI instrument has opened the THz window that contains the fundamental rotational transitions of light molecules with large electric dipole moments, such as hydrides. Hily-Blant et al. (2010a, Paper I) have detected NH, NH<sub>2</sub>, and NH<sub>3</sub> in the cold envelope of the Class 0 protostar IRAS 16293-2422. The hyperfine structures of the *N* = 1–0 transitions of NH and NH<sub>2</sub> are seen for the first time, in absorption, and allow a precise determination of their excitation temperature (*T*<sub>ex</sub>) and line centre opacity. Four lines of ammonia are also detected in absorption,

<sup>1</sup> <http://kida.obs.u-bordeaux1.fr>, <http://www.udfa.net/>, <http://www.physics.ohio-state.edu/~eric>

<sup>2</sup> <http://massey.dur.ac.uk/drf/protostellar/>

plus the fundamental rotational transition at 572 GHz with a self-absorbed line profile likely tracing both warm and cold gas. For all three molecules, excitation temperatures were found in the range 8–10 K (Paper I). The derived column density ratios are  $\text{NH}:\text{NH}_2:\text{NH}_3 = 5:1:300$ . Whilst abundances are generally too delicate to derive because the column density of  $\text{H}_2$  is uncertain, the column density ratios above provide a stringent test for the first steps of the nitrogen chemistry and for the ammonia synthesis, in particular. Indeed, the currently available nitrogen networks all produce more  $\text{NH}_2$  than  $\text{NH}$  under dark cloud conditions (Paper I), at odds with the observations.

We investigate the  $\text{NH}:\text{NH}_2$  problem in dark gas, by revisiting the kinetic rate for the reaction



We derive separate rates for reactions with p- and o- $\text{H}_2$  for which the nuclear spin  $I = 0$  and 1, respectively. In Sect. 2 we describe the new rates that are compared to experimental measurements and derive the abundances of nitrogen hydrides in typical dark cloud conditions. The results are discussed in Sect. 3 and we propose concluding remarks in Sect. 4.

## 2. Chemical modelling

### 2.1. Rate of reaction $\text{N}^+ + \text{H}_2$

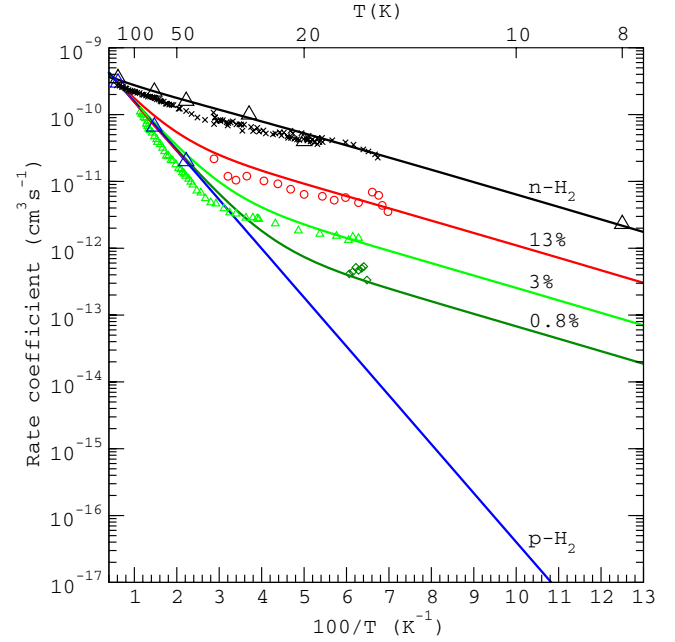
Reaction (1) has a low activation energy in the range 130–380 K (Gerlich 1993), with a consensus now tending towards a value below 200 K (e.g. Gerlich 2008). This reaction has been studied experimentally by Marquette et al. (1988), who considered pure para- $\text{H}_2$  and a 3:1 mixture of o- and p- $\text{H}_2$ , referred to as normal  $\text{H}_2$  (n- $\text{H}_2$ ). These authors fitted the two rates with normal and p- $\text{H}_2$  as  $k_n = 4.16 \times 10^{-10} \exp[-41.9/T] \text{ cm}^3 \text{ s}^{-1}$  and  $k_p = 8.35 \times 10^{-10} \exp[-168.5/T] \text{ cm}^3 \text{ s}^{-1}$ . The rate with p- $\text{H}_2$  was used by LB91, who assumed that the reaction with o- $\text{H}_2$  proceeds with no endothermicity, on the basis that the 170.51 K internal energy of the  $J = 1$  level of o- $\text{H}_2$  is used to overcome the endothermicity. Accordingly, the rate of reaction (1) was written as  $k_{\text{LB91}} = 8.35 \times 10^{-10} [x + (1-x) \exp(-168.5/T)]$ , where  $x = \text{O}/\text{P}/(1 + \text{O}/\text{P})$  is the fraction of o- $\text{H}_2$ . Actually, the expressions for  $k_n$  and  $k_p$  allows derivation of a simple expression for  $k_o$ , the reaction rate of  $\text{N}^+$  with o- $\text{H}_2$ , namely  $k_n = 3/4 k_o + 1/4 k_p$  (Gerlich 1989). For  $\text{O}/\text{P} = 3:1$  and at temperatures less than  $\approx 40$  K, the rate is essentially  $k_o$ , and  $k_n$  is thus a good approximation of  $k_o$  at the low temperatures ( $T < 15$  K) of dark clouds. Alternatively, a single-exponential fit to  $k_o$  leads to (see Fig. A.1)

$$k_o = 4.2 \times 10^{-10} (T/300)^{-0.17} \exp[-44.5/T] \text{ cm}^3 \text{ s}^{-1}. \quad (2)$$

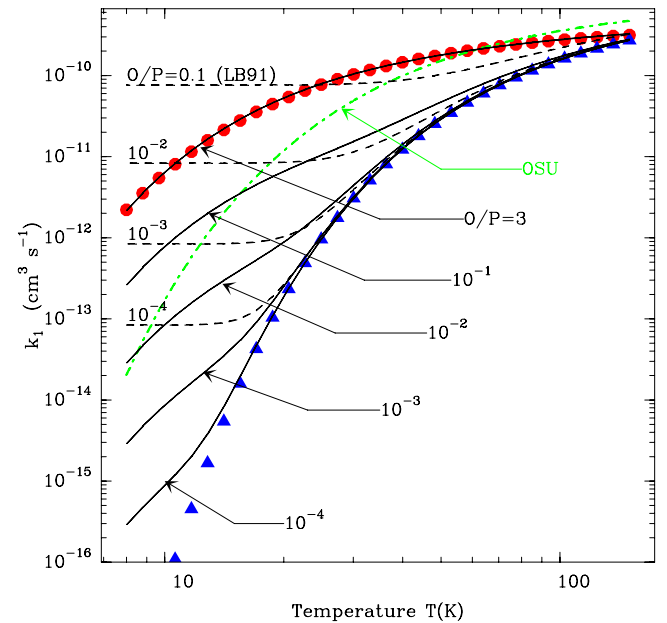
The rate for reaction (1) with an  $\text{H}_2$  admixture of arbitrary  $\text{O}/\text{P}$  is then obtained as

$$k_1 = x k_o + (1-x) k_p. \quad (3)$$

In Fig. 1, the rate  $k_1$  from Eq. (3) is compared to the experimental data of Marquette et al. (1988) for the reaction with n- $\text{H}_2$  down to 8 K and p- $\text{H}_2$  to 45 K. Gerlich (1993) performed experiments with n- $\text{H}_2$  and with p- $\text{H}_2$  containing admixtures of o- $\text{H}_2$  (13%, 8%, and 0.8%), at temperatures down to 14 K. The agreement between our Eq. (3) and the three sets of p- $\text{H}_2$  data of Gerlich (1993) is excellent at temperatures below 20 K, and to within a factor of 2 up to 100 K. This suggests that Eq. (3) should be accurate to within a factor of 2–3 down to 10 K. On the other hand, this rate should not be employed above  $\sim 150$  K.



**Fig. 1.** Comparison of the rate coefficient as given by Eq. (3) to experimental data for the reaction of  $\text{N}^+$  with n- $\text{H}_2$  and p- $\text{H}_2$  with different o- $\text{H}_2$  admixtures: 13%, 3%, 0.8%, and 0% (blue line). The small symbols are taken from Gerlich (1993) while the large triangles are CRESU results from Marquette et al. (1988). The solid lines correspond to Eq. (3) of the present paper.



**Fig. 2.** Comparison of the rate coefficient for reaction (1) as given by Eq. (3) to the rates from LB91 (dashed) and the OSU database (dot-dashed). The rates are computed for temperatures in the range 8–150 K and  $\text{O}/\text{P} = 10^{-4}, 10^{-3}, 0.01, 0.1,$  and 3 (black lines). The symbols show the fits from Marquette et al. (1988) for normal  $\text{H}_2$  (red circles,  $\text{O}/\text{P} = 3$ ) and p- $\text{H}_2$  (blue triangles).

We compare, in Fig. 2, the rate given by Eq. (3) to both  $k_{\text{LB91}}$  and to the rate given by the OSU database  $k_{\text{OSU}} = 8.35 \times 10^{-10} \exp[-85/T] \text{ cm}^3 \text{ s}^{-1}$ . The rate is computed for several values of  $\text{O}/\text{P}$ . As expected, it converges towards the n- $\text{H}_2$  and p- $\text{H}_2$  rates for high ( $\text{O}/\text{P} = 3$ ) and low ( $\text{O}/\text{P} = 10^{-4}$ ) values, respectively. It is evident that LB91 overestimated the rate

of reaction (1) by several orders of magnitude at temperatures below 20 K. In warmer gas ( $T > 20$  K),  $k_1$  and  $k_{\text{LB91}}$  agree to within a factor of 10 or less, whilst the OSU rate approaches the O/P = 3 curve. The OSU rate thus amounts to assume O/P ratios over 0.01, whereas LB91 only provides acceptable rates at temperatures larger than 20 K.

## 2.2. Abundance of nitrogen hydrides

In this work, we wish to reproduce the ratios NH:NH<sub>2</sub>:NH<sub>3</sub> observed in the cold envelope of IRAS 16293-2422 (Paper I). The fundamental hyperfine transitions of NH, NH<sub>2</sub> and several transitions of NH<sub>3</sub> have been detected in absorption. Absorption is interpreted as resulting from the low temperature of the gas in the envelope seen against the warmer continuum emitted by the dust closer to the protostar. The gas density is lower ( $10^4$ – $10^5$  cm<sup>-3</sup>) than the critical density of the detected transitions ( $>10^7$  cm<sup>-3</sup>), which ensures that collisions do not govern the (de)excitation processes. The  $N = 1$ – $0$  transitions are therefore thermalized with the dust emission temperature, which in the THz domain, corresponds to excitation temperatures close to a kinetic temperature of 10 K. The lines are Gaussian and do not show any signatures of strong dynamical effects such as infall. Dynamical timescales are then expected to be larger than the free-fall time. The observed lines therefore trace a cold gas, which is moderately dense, free of dissociating photons, and its ionization is driven by cosmic rays.

The main point raised by Paper I is that the observed ratios NH:NH<sub>2</sub>:NH<sub>3</sub> = 5:1:300 could not be reproduced by chemical networks updated for the rates of the dissociative recombination (DR) reactions leading to NH, NH<sub>2</sub>, and ammonia. Paper I considered three models, with varying branching ratios for some DR reactions. Whilst the NH<sub>2</sub>:NH<sub>3</sub> abundance ratio could be reproduced in all three cases, no model was able to produce<sup>3</sup> [NH] > [NH<sub>2</sub>]. These models used the OSU rate for reaction (1), which was shown in Sect. 2.1 to depart from the measured rate by several orders of magnitude in cold gas and O/P below 0.01. The next section explores the consequence of the new rate given by Eq. (3) on the abundances of the nitrogen hydrides in typical dark cloud conditions.

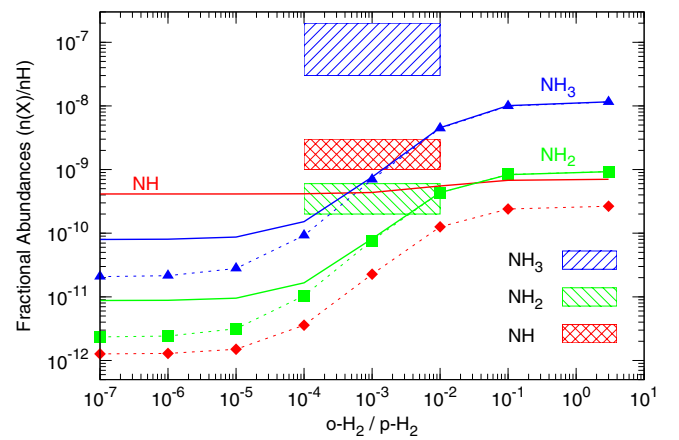
We performed chemical calculations in a gas at  $T = 10$  K, with density  $n_{\text{H}} = 10^4$  cm<sup>-3</sup>. The gas is screened by 10 mag of visual extinction, such that the ionization primarily comes from cosmic rays at an adopted rate  $\zeta = 1.3 \times 10^{-17}$  s<sup>-1</sup>. Gas-phase abundances were computed as a function of time by solving the chemical network until steady-state was reached. Freeze-out of gas-phase species onto dust grains is ignored in this work. In what follows, the quoted abundances correspond to the steady state. The initial fractional elemental abundances ( $n_{\text{X}}/n_{\text{H}}$ ) are the gas phase abundances taken from Flower & Pineau des Forêts (2003, hereafter FPdF03), who considered the depletion of metals in grain mantles, grain cores, and PAHs (see Table 1). These abundances differ from those adopted in Paper I (Wakelam & Herbst 2008). The rates for the dissociative recombination reactions are those of model 1 in Paper I. From the above, the rate for the key reaction (1) depends on the O/P, which is not known, but which might strongly differ from the thermodynamical equilibrium value (Maret & Bergin 2007; Pagani et al. 2009; Troscompt et al. 2009) which itself is  $\approx 10^{-7}$  at 10 K. The steady-state abundances of NH, NH<sub>2</sub>, and NH<sub>3</sub> were thus computed for various values of O/P in the range  $10^{-7}$  to 3.

<sup>3</sup> The fractional abundance of species X is noted [X] and equals  $n(\text{X})/n_{\text{H}}$ , with  $n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2)$ .

**Table 1.** Adopted initial gas phase fractional abundances ( $n(\text{X})/n_{\text{H}}$ ) with  $n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2)$ .

Species	This work <sup>a</sup>	Wakelam 2008 <sup>b</sup>
H <sub>2</sub>	0.50	0.50
He	0.10	0.14
N	6.39(−5)	2.14(−5)
O	1.24(−4)	1.76(−4)
C <sup>+</sup>	8.27(−5)	7.30(−5)
S <sup>+</sup>	1.47(−5)	8.00(−8)
Si <sup>+</sup>	8.00(−9)	8.00(−9)
Fe <sup>+</sup>	3.00(−9)	3.00(−9)
Mg <sup>+</sup>	7.00(−9)	7.00(−9)

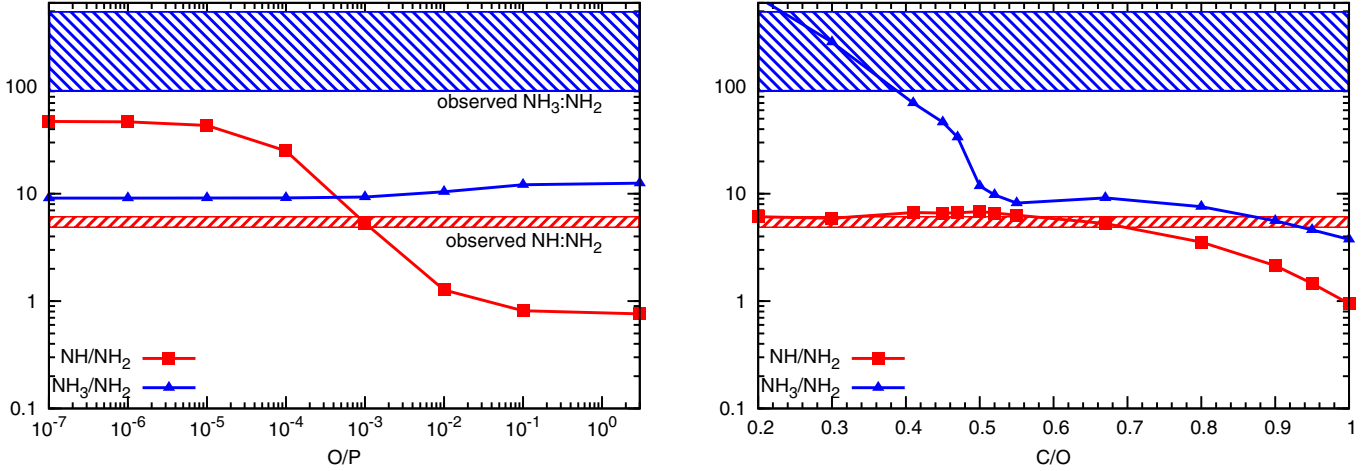
**Notes.** Numbers in parentheses are powers of 10. <sup>(a)</sup> Flower & Pineau des Forêts (2003). <sup>(b)</sup> Low-metal model from Wakelam & Herbst (2008).



**Fig. 3.** Steady-state abundances (with respect to H nuclei) of nitrogen hydrides as a function of O/P, in a 10 K gas with  $n_{\text{H}} = 10^4$  cm<sup>-3</sup>, and  $\zeta = 1.3 \times 10^{-17}$  s<sup>-1</sup>. The rate of reaction (1) is given by Eq. (3). Two branching ratios for the channel  $\text{N}_2\text{H}^+ + \text{e}^- \rightarrow \text{NH} + \text{N}$  are considered: 0% (dashed lines) and 10% (full lines). The observed abundances from Paper I are also indicated (filled rectangles).

In this work, the DR of  $\text{NH}_4^+$  has three output channels,  $\text{NH}_3 + \text{H}$ ,  $\text{NH}_2 + \text{H}_2$ , and  $\text{NH}_2 + \text{H} + \text{H}$  (Öjekull et al. 2004). However, another channel may be  $\text{NH} + \text{H} + \text{H}_2$  (Adams et al. 1991), but to our knowledge, no branching ratio is available in the literature. Values up to 10% may be considered in a future work.

We first consider the case where the DR of  $\text{N}_2\text{H}^+$  produces only  $\text{N}_2 + \text{H}$  (Adams et al. 2009). The resulting abundances are shown in Fig. 3. It appears that the O/P controls the abundances of NH, NH<sub>2</sub>, and NH<sub>3</sub> but the ratios NH:NH<sub>2</sub> and NH<sub>3</sub>:NH<sub>2</sub> are insensitive to O/P. In a second series of calculations, the  $\text{NH} + \text{N}$  channel is given a 10% branching ratio for the DR of  $\text{N}_2\text{H}^+$ . In this case, the abundance of NH is nearly independent of O/P, while the abundances of NH<sub>2</sub> and NH<sub>3</sub> remain unaffected. As a consequence, it is found that  $\text{NH} : \text{NH}_2 > 1$  for  $\text{O}/\text{P} < 0.03$ . In Paper I, though, opening this channel did not solve the NH:NH<sub>2</sub> problem, which contrasts with the above result. This may be understood as follows. When the  $\text{NH} + \text{H}$  channel of the dissociative recombination of  $\text{N}_2\text{H}^+$  is opened with a 10% branching ratio, the corresponding rate is  $\approx 5.5 \times 10^{-8}$  cm<sup>3</sup> s<sup>-1</sup>, several orders of magnitude higher than  $k_1$  (see Fig. 2). This channel, which is insensitive to O/P, therefore dominates the formation of NH over  $\text{NH}_2^+ + \text{e}^-$ . In contrast, the other hydrides NH<sub>2</sub> and NH<sub>3</sub> are daughter molecules of  $\text{NH}^+$ , which is formed



**Fig. 4.** Abundance ratios calculated when a 10% branching ratio is considered for the reaction  $\text{N}_2\text{H}^+ + \text{e}^- \rightarrow \text{NH} + \text{H}$ . The hashed bands show the observed ratios with their  $1\sigma$  uncertainties. *Left panel:* varying O/P, with the initial abundances of Flower & Pineau des Forêts (2003) ([O] = 1.24(−4) and [C] = 8.27(−5)). *Right panel:* varying [O] while keeping [C] constant, at constant O/P =  $10^{-3}$ . The low-metal abundances of Wakelam & Herbst (2008) are [O] = 1.76(−4) and [C] = 7.30(−5), or C:O = 0.41.

from  $\text{N}^+ + \text{H}_2$  whose rate does explicitly depend on O/P in the present work. Hence the abundances of  $\text{NH}$  and  $\text{NH}_3$  do also depend on O/P. On the other hand, at the temperature of 10 K and  $\text{O/P} < 10^{-3}$ , the revised rate  $k_1$  (Eq. (3)) is at least an order of magnitude lower than the OSU rate used in Paper I. For greater O/P, the rate is similar to or even higher, up to a factor of 10. These two effects, namely the drop of  $k_1$  for low O/P, and the O/P-independent formation of  $\text{NH}$ , makes it possible to produce an  $\text{NH}:\text{NH}_2$  ratio with values above unity. In the following we keep the  $\text{NH} + \text{N}$  channel opened to 10% and explore some consequences of this result.

### 3. Discussion

#### 3.1. The $\text{H}_2$ O/P ratio in dark clouds

Computing the abundance ratios  $\text{NH}:\text{NH}_2$  and  $\text{NH}_3:\text{NH}_2$  for different O/P ratios leads to the left panel of Fig. 4. The initial fractional abundances are kept fixed, while the rate of reaction (1) is calculated for values of O/P from  $10^{-7}$  (close to the Boltzmann value at 10 K) to 3. The calculated ratios are compared with the observational constraints. As expected, the  $\text{NH}_3:\text{NH}_2$  ratio is insensitive to O/P variations. It is equal to ten, which is inconsistent with the observed value of 300. In contrast, the  $\text{NH}:\text{NH}_2$  ratio shows two regimes: for  $\text{O/P} < 10^{-5}$ ,  $\text{NH}:\text{NH}_2 \approx 50$ , and for  $\text{O/P} > 0.1$ ,  $\text{NH}:\text{NH}_2 \approx 0.07$ . The observed ratio of 5 is intermediate, and indeed it constrains the O/P to  $10^{-3}$  well. From Fig. 4, we conclude that there is a range of O/P for which  $[\text{NH}] > [\text{NH}_2]$  and  $[\text{NH}] < [\text{NH}_3]$  simultaneously. In our case, this range is  $\text{O/P} = 5 \times 10^{-4} - 0.02$ . The O/P ratio appears as a control parameter for the  $\text{NH}:\text{NH}_2$  ratio, and allows for the first time more  $\text{NH}$  than  $\text{NH}_2$  to be produced. Conversely, the measure of  $\text{NH}:\text{NH}_2$  tightly constrains the O/P ratio. We note that the fractional abundance of  $\text{NH}_3$  of  $1.9 \times 10^{-9}$ , measured by Crapsi et al. (2007) towards the starless core L 1544, corresponds to an  $\text{O/P} = 10^{-3}$  to  $10^{-2}$ . This ratio is a factor of 10 larger than the corresponding ratio from the model of LB91. It is thus found that reaction (1) regulates the formation of  $\text{NH}_2$  and  $\text{NH}_3$  whilst the formation of  $\text{NH}$  is controlled by the dissociative recombination of  $\text{N}_2\text{H}^+$  provided the branching ratio towards  $\text{NH}$  is 10%. The value of this branching ratio is uncertain but is likely non-zero (Adams et al. 2009).

#### 3.2. Dependence on the initial abundances

The  $\text{NH}_3:\text{NH}_2$  ratio is  $\approx 10$  in the above models, a factor 30 below the observed values towards IRAS 16293-2422. However, models computed in Paper I with the initial abundances of Wakelam & Herbst (2008) lead to a ratio close to the observed value, thus suggesting that the initial elemental abundances influence this ratio. The gas phase elemental abundances of C, N, and O in dark clouds are poorly known because the amount of these elements incorporated into the dust (core or mantles) is loosely constrained. The elemental abundance of oxygen in the gas phase is not known accurately, and variations by an order of magnitude are fully conceivable (Jenkins 2009), whilst that of carbon is better known. Accordingly, we have considered variations in the initial elemental abundances of oxygen, to vary the ratio C:O, encompassing the value of 0.41 from Wakelam & Herbst (2008).

The resulting abundance ratios, computed for an O/P ratio of  $10^{-3}$ , are shown in Fig. 4 (right panel). As C:O decreases below the 0.66 value of FPDF03, the ratio  $\text{NH}_2:\text{NH}_3$  increases. In the process,  $\text{NH}:\text{NH}_2$  remains constant. When C:O is now increased above 0.66, both ratios decrease, by at most a factor 2 to 5. It is thus apparent that, when [O] is increased, the C:O ratio controls the  $\text{NH}_2:\text{NH}_3$  ratio. On chemical grounds, the C:O ratio is expected to influence the abundance of  $\text{NH}_2$ , for which the main destruction routes involve oxygen to form  $\text{NO}$ ,  $\text{NH}$ , and  $\text{HNO}$ . Similarly,  $\text{NH}$  is mostly removed by reaction with oxygen to principally form  $\text{NO}$ . However, when oxygen is significantly depleted from the gas phase ( $\text{C:O} > 0.5$ ), another destruction route of  $\text{NH}$ , involving sulphur, becomes important. As a result, the  $\text{NH}:\text{NH}_2$  ratio is mostly insensitive to C:O, until  $\text{C:O} > 0.5$  when it starts to decrease by small factors. The situation is different for  $\text{NH}_3$  which is destroyed by charge transfer reactions with  $\text{H}^+$  and  $\text{S}^+$  and by proton exchange reactions with  $\text{H}_3^+$  and  $\text{HCO}^+$ , forming notably  $\text{NH}_4^+$ , which dissociates back into  $\text{NH}_3$ , and  $\text{NH}_3^+$ . A fraction of  $\text{NH}_3^+$  will lead to  $\text{NH}_2$  and  $\text{NH}$  which are the true destruction channels of ammonia. The abundance of  $\text{NH}_3$  is thus only marginally affected by the change in C:O. Consequently, as C:O decreases below 0.66,  $\text{NH}:\text{NH}_2$  keeps constant and  $\text{NH}_3:\text{NH}_2$  increases by more than one order of magnitude. Whereas when C:O increases,  $\text{NH}:\text{NH}_2$  decreases

by less than a factor 10, whilst NH<sub>3</sub>:NH<sub>2</sub> is approximately constant.

#### 4. Conclusions

Using an updated rate for reaction (1) with an explicit dependence on the O/P ratio, we have shown that the O/P of H<sub>2</sub> controls the ratio NH:NH<sub>2</sub> in dark clouds without affecting the NH<sub>3</sub>:NH<sub>2</sub> ratio. A value of O/P close to 10<sup>-3</sup> leads to NH : NH<sub>2</sub> > 1 and NH<sub>3</sub> : NH<sub>2</sub> < 1 as observed. Interestingly, this value of O/P is close to the predictions of Flower et al. (2006, their Fig. 1) under similar conditions. In addition, measuring the NH:NH<sub>2</sub> ratio may be a new method of constraining the O/P ratio of H<sub>2</sub> in dark clouds. We also showed that decreasing the C:O ratio by increasing [O] controls the NH<sub>2</sub>:NH<sub>3</sub> ratio. Finally, acceptable parameters were found that lead to abundance ratios in agreement with the observations towards IRAS 16293-2422, namely O/P ≈ 10<sup>-3</sup> and C:O ≤ 0.4. It was noted, however, that in this range of parameters, the absolute abundances predicted by the models are a factor of 10 below those derived in Paper I.

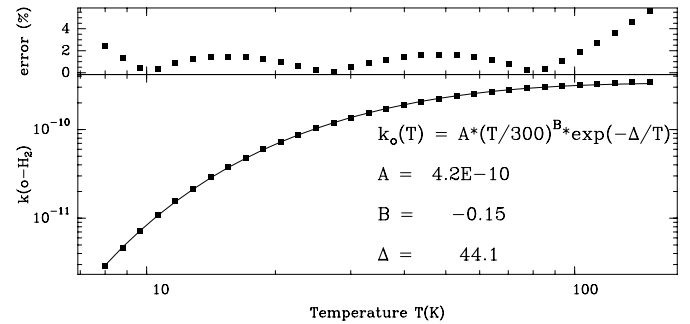
In this work, the influence of O/P on the ratios NH:NH<sub>2</sub>:NH<sub>3</sub> was only explored through the rate of reaction (1). A better study would be to self-consistently compute the O/P ratio from a model of conversion of o-H<sub>2</sub> into p-H<sub>2</sub>, as was first considered by LB91 and, more recently, by e.g. Pagani et al. (2009). Including proton exchange reactions, in the gas phase, between H<sub>2</sub> and H<sup>+</sup> (Honvault et al. 2011), H<sub>2</sub><sup>+</sup> (Crabtree et al. 2011), and H<sub>3</sub><sup>+</sup> (Hugo et al. 2009) would reprocess the 3:1 mixture of H<sub>2</sub> formed on grains to a different O/P. An even more self-consistent approach would be that of Flower et al. (2006) who separate the reactions with the ortho- and para-forms of all concerned N-bearing molecules. Another obvious continuation would be to explore these findings in different physical conditions (A<sub>v</sub>, cosmic-ray ionization rate, etc.).

Branching ratios of dissociative recombination reactions are crucial to the formation of nitrogen hydrides. In this work, the dissociative recombination of NH<sub>4</sub><sup>+</sup> has three output channels NH<sub>3</sub> + H, NH<sub>2</sub> + H<sub>2</sub>, and NH<sub>2</sub> + H + H (Öjekull et al. 2004). However, another channel may be NH + H + H<sub>2</sub> (Adams et al. 1991), but to our knowledge, no branching ratio is available in the literature. Values up to 10% may be considered in a future work. Critical too are the values of rates at low temperatures, especially for reaction (1) with p-H<sub>2</sub> for which measurements at temperatures lower than 14 K are not available.

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#### Appendix A: Reaction rate

For the purpose of implementing the rate of the reaction (1) with ortho-H<sub>2</sub> in chemical networks, Fig. A.1 shows the result of a single-exponential fit. The filled squares are



**Fig. A.1.** Rate for reaction (1) with o-H<sub>2</sub> and fit result (see Eq. (2)). *Bottom panel:* filled squares are the values derived from Marquette et al. (1988), and the fitted curve (full line). *Top panel:* relative error.

based on the fitted reaction rates from Marquette et al. (1988). A weighting in the form 1/(T - 10)<sup>2</sup> was adopted, which is accurate to better than 6% for T = 8–150 K.

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